

Composition, stability, and structure of Cu(II), Ni(II), and Co(II) complexes with adipic acid dihydrazide in aqueous and aqueous-ethanol solutions

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Abstract

Solvation and complexation of Cu(II), Ni(II), and Co(II) with adipic acid dihydrazide (L) in aqueous and aqueous-ethanol solutions (ethanol mole fraction 0.07-0.68) were studied by spectrophotometry. The formation constants of the species $M(LH)_3^{3+}$, ML_2^{2+} , $M_2L_4^{4+}$ ($\mu = Cu^{2+}$, Ni^{2+} , Co^{2+}), and also $M_2L_2^{4+}$ and ML_2^{2+} ($\mu = Cu^{2+}$, Ni^{2+}) were determined. With Cu(II), the complexes $Cu(LH)_2^{4+}$, $CuL(LH)_3^{3+}$, and $Cu_2L(LH)_5^{5+}$ were also detected and characterized. Evidence is given for the hydrazide coordination mode: tridentate in ML_2^{2+} , bidentate in $M(LH)_3^{3+}$ and ML_2^{2+} , and tetradentate in $M_2L_4^{4+}$ and $M_2L_2^{4+}$. The ligand exchange reactions involving CuL_2^{2+} , $Cu(LH)_3^{3+}$, $Cu(LH)_2^{4+}$, $CuL(LH)_3^{3+}$, CuL_2^{2+} , and $Cu_2L(LH)_5^{5+}$ in aqueous solutions of Cu(II) were revealed and kinetically characterized by nuclear magnetic relaxation. The heretofore unknown rate constants of formation of these complexes were calculated from the thermodynamic and kinetic parameters. Factors controlling the rate constants of the complex formation and chemical exchange are discussed. © Pleiades Publishing, Inc., 2006.

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